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USE OF A REACTION RATE METHOD TO PREDICT FAILURE TIMES OF ADHESIVE BONDS AT CONSTANT STRESS

ELISE McABEE
DAVID W. LEVI

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PICATINNY ARSENAL
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by

Elise McAbee
David W. Levi

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Materials Engineering Laboratory
Feltman Research Laboratories
Picatinny Arsenal
Dover, N. J.

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OBJECT

The object of this work was to determine whether a reaction rate method could be used to predict failure times of adhesive bonds under constant stress conditions.

SUMMARY

A reaction rate method was successfully used to predict failure times for adhesive bonds under constant stress at 90-95% and at 50% relative humidity. The method was found to be not very useful when the experiments were performed at 20% relative humidity. The results suggest that the method should be particularly useful under high humidity, bond-degrading conditions such as exist in the tropics.

INTRODUCTION

Tobolsky and Eyring (Ref 1) first considered the lifetime of a material subjected to mechanical restraint to be a process according to a rate equation. Application of reaction rate theory to polymer mechanical behavior has been reported by a number of investigators (Refs 2 to 5). Recently, it has been shown that such a treatment is applicable to some adhesive data under constant rate of loading conditions (Ref 6). In the present report, an attempt is made to apply these ideas to some data from constant stress measurements of the strength of adhesive bonds.

RESULTS AND DISCUSSION

The constant stress data was obtained with Sharpe jigs (Ref 9) at the various temperatures and humidities listed later in this report. Details of the experiments will be published in a subsequent report (Ref 7). Failures were predominantly cohesive within the adhesive layer although there is some indication that the percent cohesive failure decreases with increasing time to failure regardless of the temperature or relative humidity (Ref 7).

It has been shown (Refs 2, 4, and 8) that, by integrating the rate equation and making certain reasonable assumptions, it is possible to obtain an expression of the form:

$$\log t_f = C - \log T + \frac{\Delta H^{\neq}}{2.3RT} - b\frac{S}{T} \qquad (1)$$

where t_f is failure time

C and b are constants

T is absolute temperature

$\Delta H^{\neq}/2.3RT$ is an activation energy term

S is the stress.

At constant temperature, the experimental data should give a straight line according to

$$\log t_f = D - b \frac{S}{t} . \qquad (2)$$

The apparent activation energy may then be evaluated by extrapolating several constant temperature lines to the vertical intercept (S/T = 0) and plotting according to

$$\log t_f = \frac{\Delta H\neq}{2.3RT} + C. \qquad (3)$$

If the above reasoning is valid, the data should give a straight line passing through the origin when plotting according to

$$\log \frac{t_f T}{C} - \frac{\Delta H\neq}{2.3RT} = b \frac{S}{T} . \qquad (4)$$

An alternative procedure has been worked out (Ref 6) for cases where isothermal data is lacking. In such cases, if we multiply Equation 1 through by T and consider a data point t_f and S_1 at T_1, we obtain

$$T_1 \log t_{f1} T_1 = CT_1 + \frac{\Delta H\neq}{2.3R} - b S_1 . \qquad (5)$$

We may then write a similar expression for t_{f_2}, S_2 and T_2:

$$T_2 \log t_{f2} T_2 = CT_2 + \frac{\Delta H\neq}{2.3R} - b S_2 . \qquad (6)$$

Assuming the constancy of $\Delta H \neq$

$$\frac{\Delta H \neq}{2.3R} = T_1 \log t_{f_1} T_1 - CT_1 + b S_1 = T_2 \log t_{f2} T_2 - CT_2$$

$$+ b S_2 \qquad (7)$$

Rearranging and dividing through by $T_1 - T_2$, we obtain

$$\frac{T_1}{T_1 - T_2} \log t_{f_1} T_1 - \frac{T_2}{T_1 - T_2} \log t_{f_2} T_2 = C + b \frac{(S_2 - S_1)}{(T_1 - T_2)} \quad (8)$$

For every possible pair of data points, the left hand side of Equation 8 may be plotted against $(S_2-S_1)/(T_1-T_2)$. C and b may then be evaluated as the intercept and slope, respectively. After C and b are determined, we may go back to Equation 1 in the form

$$\log t_f T - C + b \frac{S}{T} = \frac{\Delta H \neq}{2.3RT} \quad (9)$$

The left hand side of Equation 9 is plotted against $1/T$ to evaluate $\Delta H \neq$.

Table 1 shows the data for an AF126 adhesive with aluminum adherends (Ref 7) at 90 - 95% relative humidity. In each case, at least 4 samples were loaded at each stress indicated. The table gives average failure times. As may be expected for adhesive data, the scatter was quite pronounced. Details of the scatter will be published later (Ref 7).

In order to evaluate the parameters considered in the reaction rate equations, the data was plotted in two ways. Figure 1 shows a plot according to Equation 2. A second plot, in accord with Equation 8, is given in Figure 2. Arrhenius plots for the evaluation of $\Delta H \neq$ are shown in Figure 3. After evaluation of parameters, the following final equations relating failure time to stress and temperature were arrived at:

Method I, based on Equations 2 and 3

$$\log t_f = 7.4 + 5130 (1/T) - \log T - 0.45 (S/T) \quad (10)$$

Method II, Two-Point Method

$$\log t_f = 8.07 + 5300 (1/T) - \log T - 0.45 (S/T) \quad (11)$$

A least squares method was used to determine the line in Figure 2. The correlation coefficient was 0.90. The value b = 0.45 was then used to draw the lines in Figure 1. The fit to the data appears to be quite good. From Equations 10 and 11, it is noted that $H \neq = 24$ k cal by both methods. Using two methods of data treatment in this way does give added confidence in the results.

Equations 10 and 11 were used to calculate failure times for each of the experimental points given in Table 1. Results of the calculations are shown in Table 2 where they are compared with the experimental values. Taking into account the usual scatter of adhesive mechanical property data, the agreement between experimental and calculated values is considered to be quite good.

To get an independent test of the validity of Equations 10 and 11 for estimating lifetimes of bonds with AF126 adhesive, a series of experiments was performed at a different temperature (333°K) and the experimental lifetimes were compared with those calculated in terms of Equations 10 and 11. Table 3 gives the results. The reasonably good agreement found by such an independent experiment gives further confidence in the validity of the treatment.

Comparable constant stress experiments with the same adhesive and adherends were also performed at 50% and at 20% relative humidity. Table 4 shows the data and Figures 4 and 5 show the plots for 50% relative humidity according to the two methods outlined above. In this case, the scatter is somewhat more troublesome than for the higher humidity. A visual comparison of Figures 2 and 5 indicates that the results in the latter case are not as good. The correlation coefficient for the line (least squares) in Figure 5 is 0.86. Figure 6 shows the Arrhenius plots for the two methods. In both cases, apparent activation energy is 41 k cal for the higher humidity. Apparently the environment has a considerably less weakening effect on the bond at the lower humidity. Then a higher energy is required to cause rupture. It seems reasonable that a greater scatter would result at lower humidities, since the lack of bond weakening by moisture would make random flaws more important in the failure process.

For 50% relative humidity the equations relating failure time to stress and temperature are:

Method I, based on Equations 2 and 3:

$$\log t_f = -22.45 + 11{,}000\,(1/T) - \log T - 0.71\,(S/T) \quad (12)$$

Method II, Two-Point Method:

$$\log t_f = -22.06 + 11{,}000\,(1/T) - \log T - 0.71\,(S/T) \quad (13)$$

Equations 12 and 13 were used to obtain the calculated log t_f values shown in Table 5.

The results of the 20% relative humidity experiments are shown in Table 6 and in Figures 7 and 8. The correlation coefficient for the least squares line in Figure 8 is only 0.54. The positions of possible lines in Figure 7 are also quite uncertain. It appears that the reaction rate method is not useful in this case. As was mentioned earlier in this report, longer failure times tend to give more adhesive failure. For the lower humidities considerably higher stresses must be used to give reasonably short time failures. In addition, at lower humidities there should not be as much environmental weakening of bonds and hence random flaws probably play a more prominent role. Thus, it appears that a combination of several reasons may have caused the failure of the method at low humidity.

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TABLE 1

Failure data for AF126 adhesive (aluminum adherends) under constant stress

Temperature, ^{o}K	t_f, min	S, psi	Relative Humidity (RH), %
296	533	3080	90
	4,320	2600	
	10,080	2200	
	38,880	1760	
322	15,840	1760	95
	19,440	1540	
	23,760	1320	
	9,360	1100	
	64,800	880	
344	860	1760	95
	900	1540	
	3,756	1320	
	2,700	1100	
	6,900	880	
	248	1980	
	308	1760	
	214	1540	

TABLE 2

Comparison of calculated and experimental failure times at 90-95% relative humidity

T, °K	S, psi	Exptl log t_f, min	Calcd log t_f, min Method I (Eq 10)	Calcd log t_f, min Method II (Eq 11)
296	3080	2.73	2.78	2.68
	2600	3.64	3.51	3.41
	2200	4.00	4.12	4.02
	1760	4.59	4.78	4.68
322	1760	4.20	3.56	3.42
	1540	4.29	3.87	3.73
	1320	4.38	4.18	4.03
	1100	3.97	4.48	4.34
	880	4.81	4.79	4.65
344	1760	2.94	2.67	2.50
	1540	2.95	2.96	2.79
	1320	3.58	3.24	3.07
	1100	3.43	3.53	3.36
	880	3.84	3.82	3.65
	1980	2.39	2.38	2.21
	1760	2.49	2.67	2.50
	1540	2.33	2.96	2.79

TABLE 3

Comparison of calculated and experimental failure times at 333°K and 90-95% relative humidity

S, psi	Exptl log t_f, min	Calcd log t_f, min Method I (Eq 10)	Calcd log t_f, min Method II (Eq 11)
1540	3.85	3.39	3.23
1760	3.55	3.09	2.93
1980	2.75	2.79	2.63
2200	2.14	2.50	2.34
2420	2.26	2.20	2.04

TABLE 4

Failure data for AF126 adhesive (aluminum adherends) under constant stress at 50% relative humidity

Temperature, ^{o}K	t_f, min	S, psi
322	18,720	2420
	6,300	2640
	340	2860
333	11,200	1760
	7,510	1980
	1,150	2200
	350	2420
344	14,200	1320
	10,720	1540
	4,620	1760
	300	1980
	610	2200

TABLE 5

Comparison of calculated and experimental failure times at 50% relative humidity

T, °K	S, psi	Exptl log t_f, min	Calcd log t_f, min Method I (Eq 12)	Calcd log t_f, min Method II (Eq 13)
322	2420	4.27	3.87	4.26
	2640	3.80	3.39	3.78
	2860	2.53	2.90	3.29
333	1760	4.05	4.31	4.70
	1980	3.88	3.84	4.23
	2200	3.06	3.37	3.76
	2420	2.54	2.90	3.29
344	1320	4.15	4.27	4.66
	1540	4.03	3.81	4.20
	1760	3.67	3.36	3.75
	1980	2.48	2.90	3.29
	2200	2.79	2.45	2.84

TABLE 6

Failure data for AF126 adhesive (aluminum adherends) under constant stress at 20% relative humidity

Temperature, ^{o}K	t_f, min	S, psi
322	11,340	2420
	490	2640
	150	2860
	260	3080
	230	3300
333	56	2200
	130	2420
	153	2640
	147	2860
	28	3000
344	720	1760
	490	1980
	160	2200
	110	2420
	75	2640

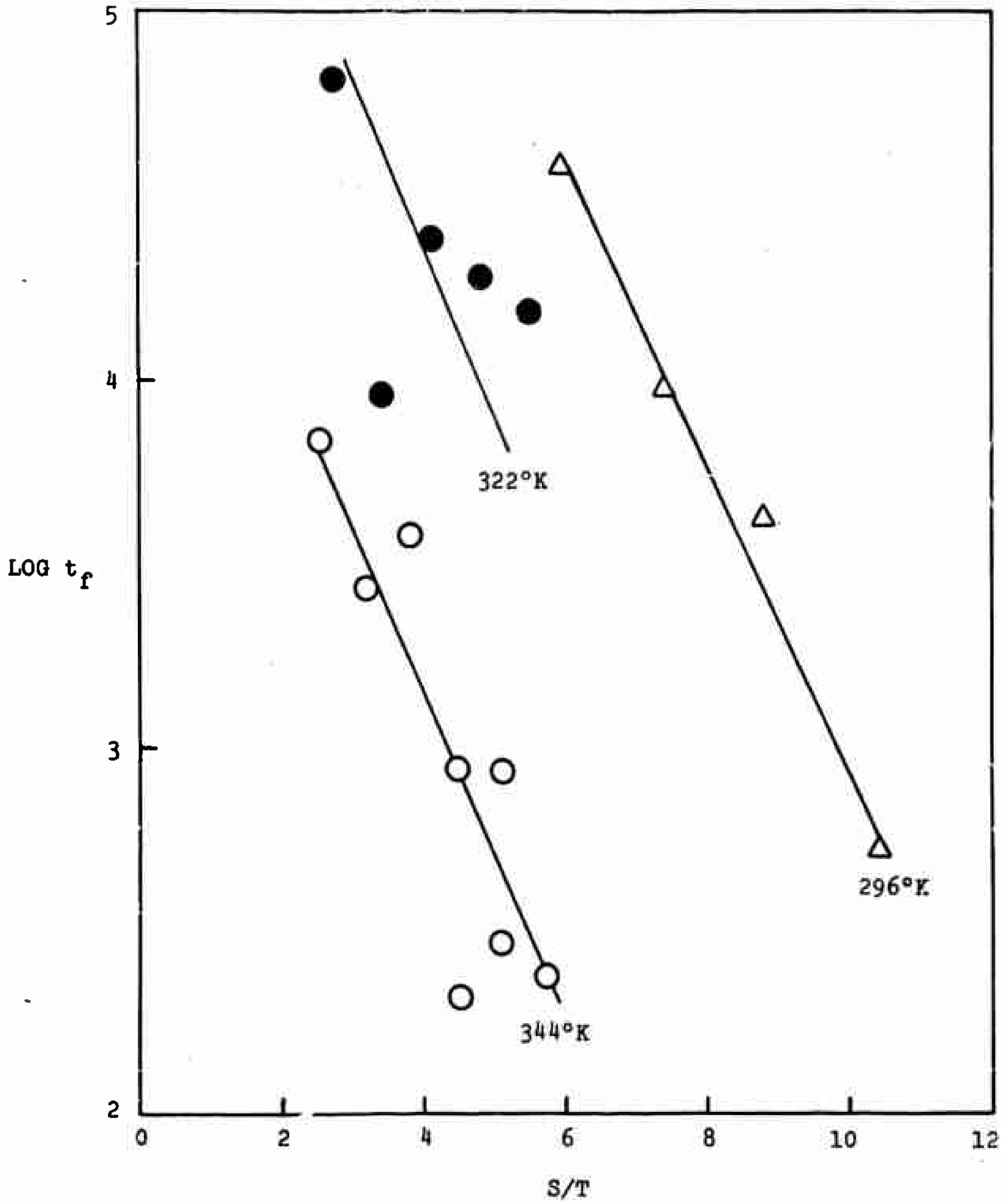

Fig 1 Log t_f vs S/T for AF126 adhesive (aluminum adherends) under constant stress at 90-95% relative humidity

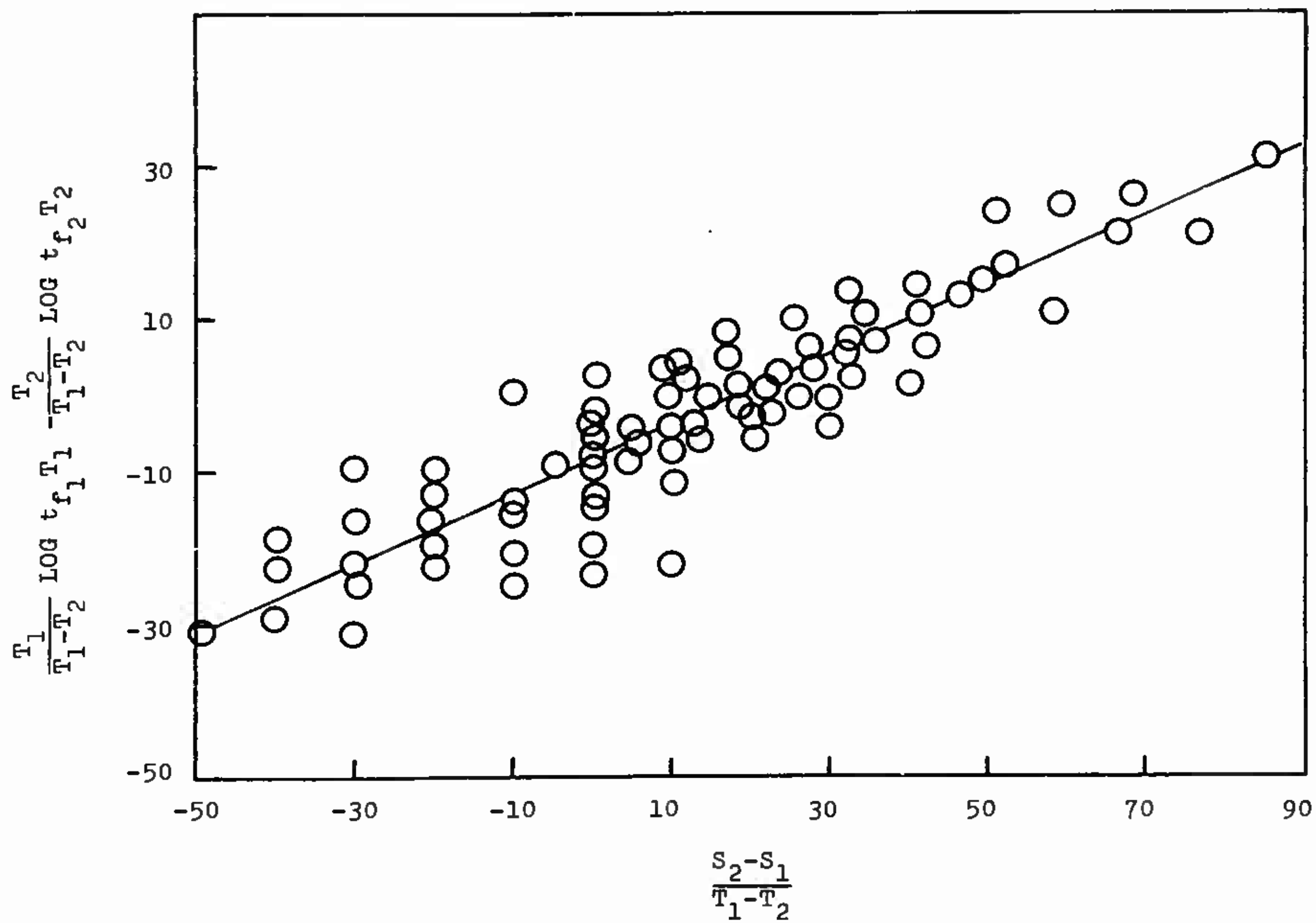

Fig 2 The data for AF126 adhesive at 90-95% relative humidity plotted according to Equation 8

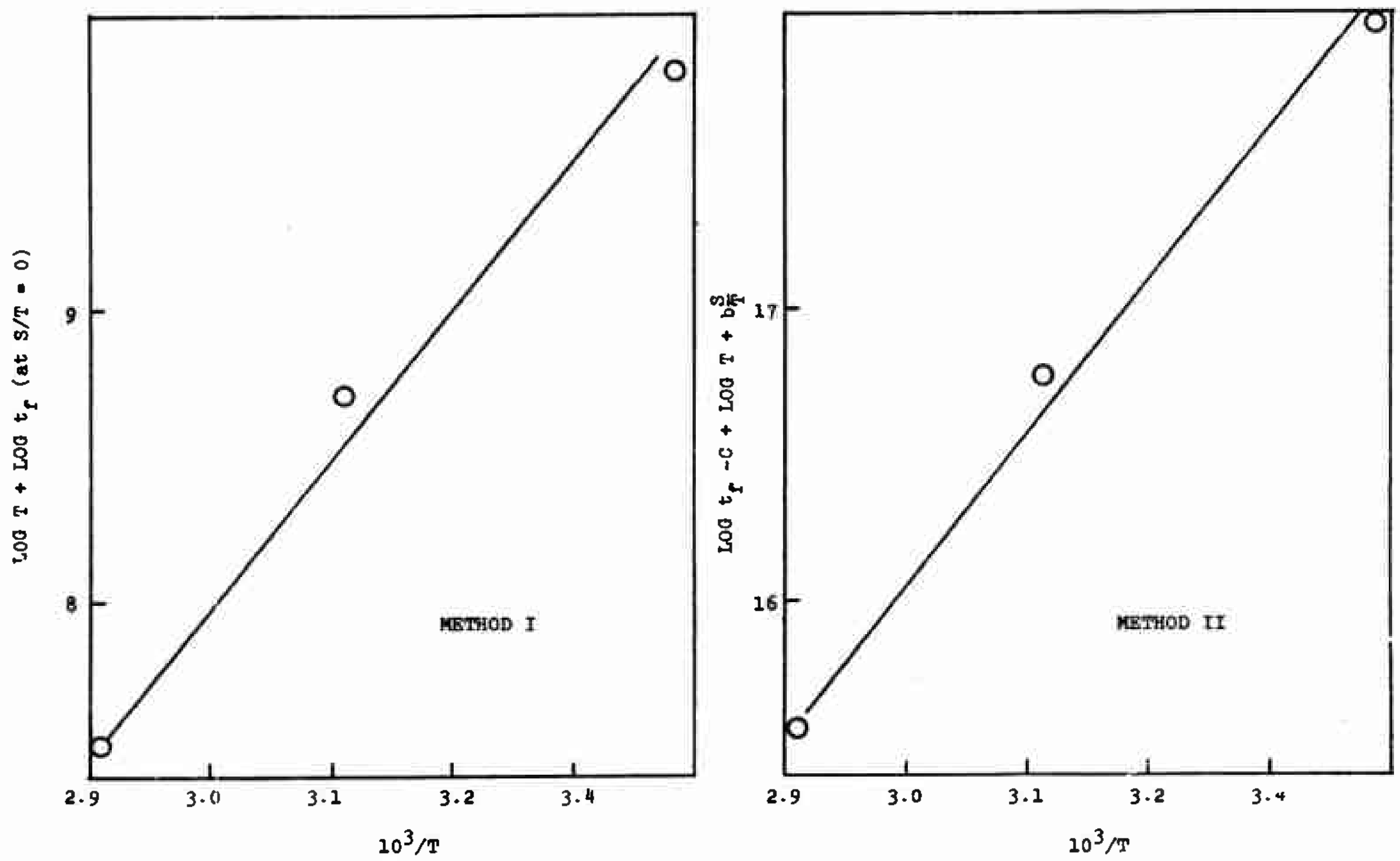

Fig 3 Arrhenius plots for evaluation of $\Delta H \neq$ at 90-95% relative humidity

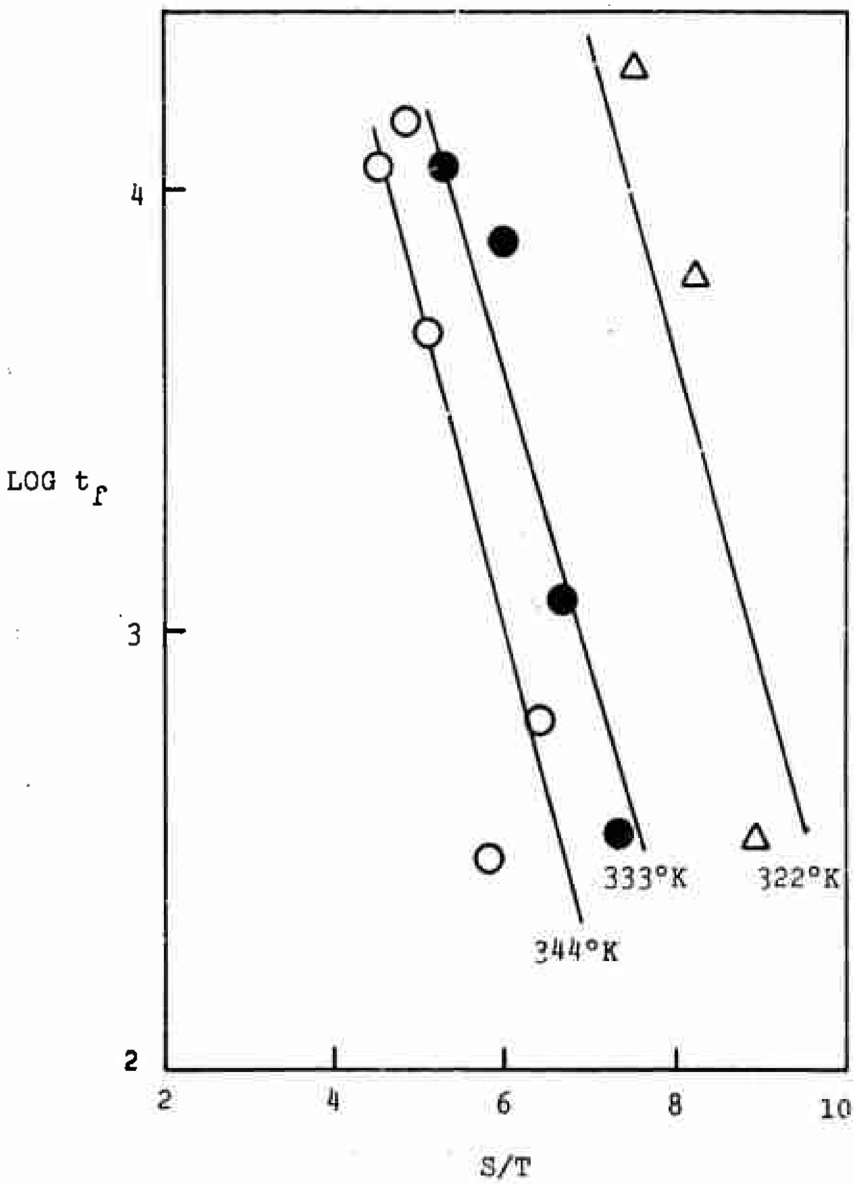

Fig 4   Log t_f vs S/T for AF126 adhesive (aluminum adherends) under constant stress at 50% relative humidity

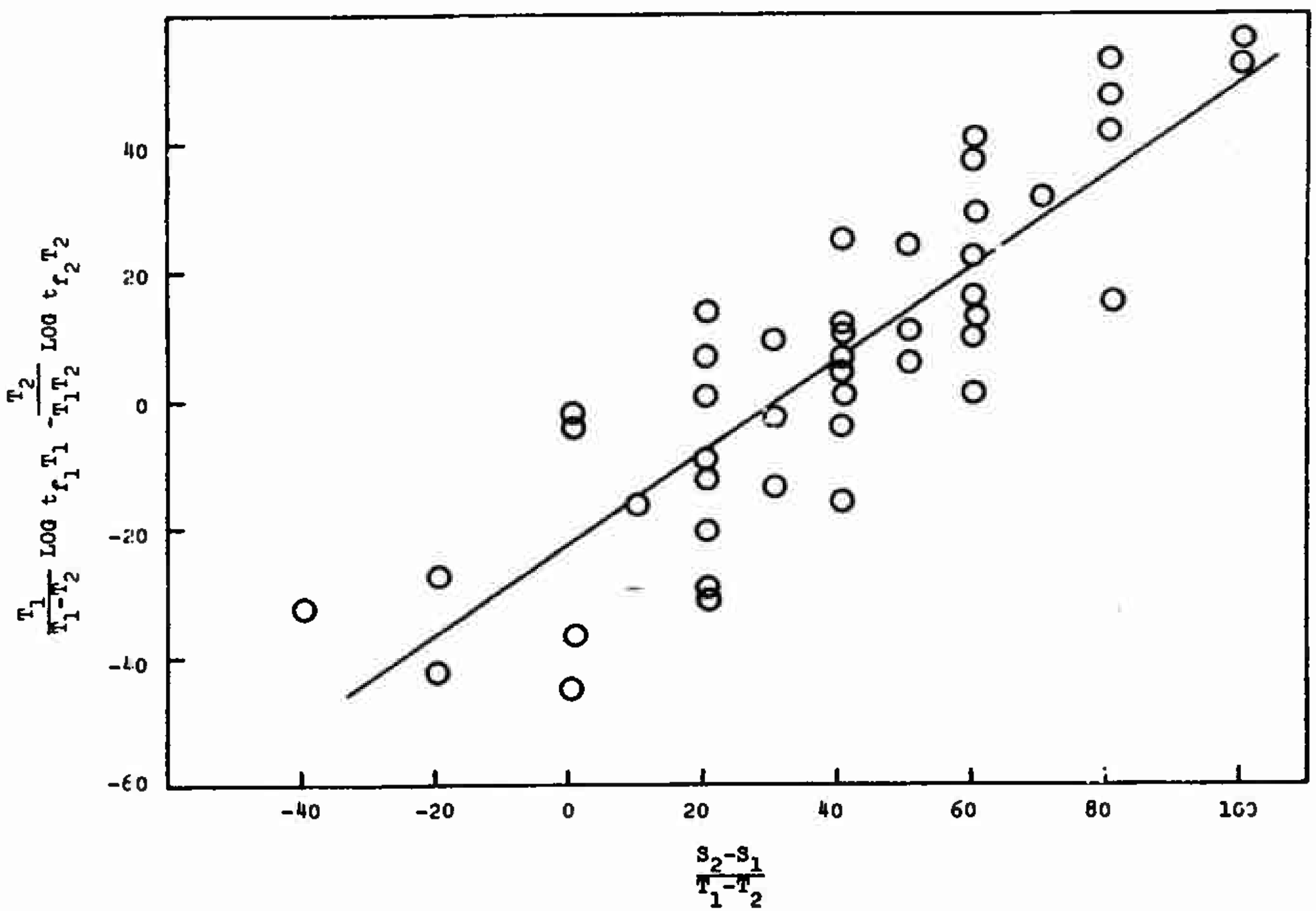

Fig 5 The data for AF126 adhesive at 50% relative humidity, plotted according to Equation 8

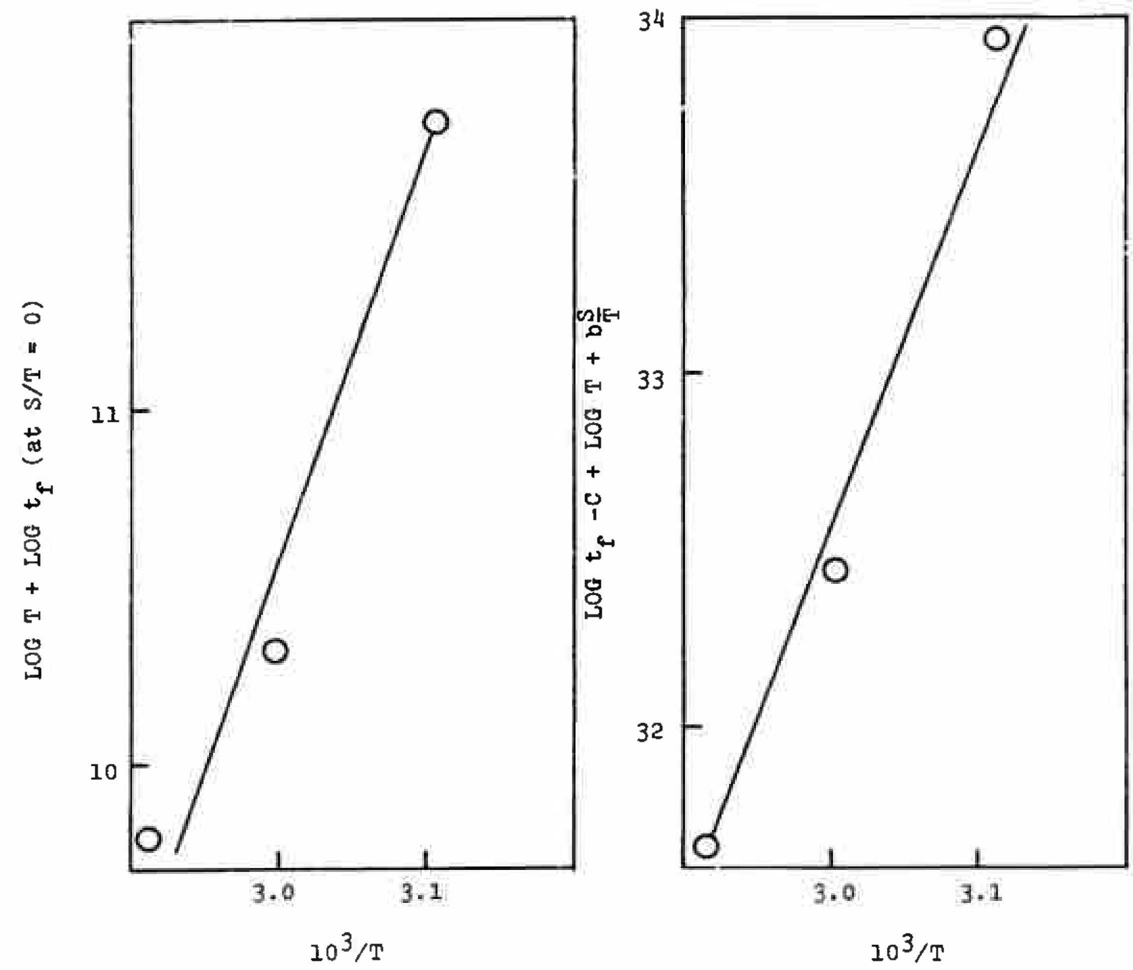

Fig 6 Arrhenius plots for evaluation of $\Delta H \neq$ at 50% relative humidity

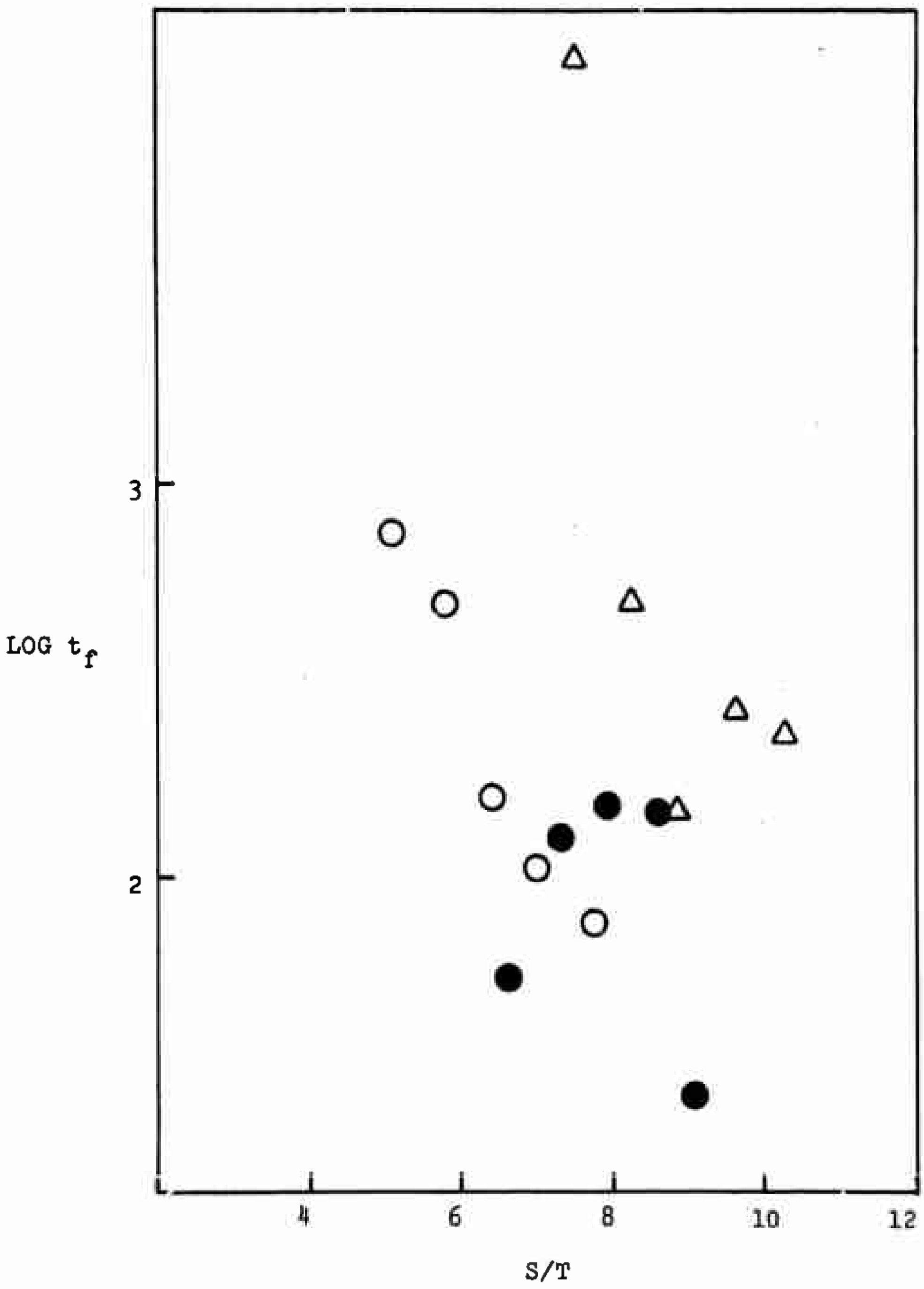

Fig 7 Log t_f vs S/T for AF126 adhesive (aluminum adherends) under constant stress at 20% relative humidity (△ = 322°K; ● = 333°K; O = 344°K)

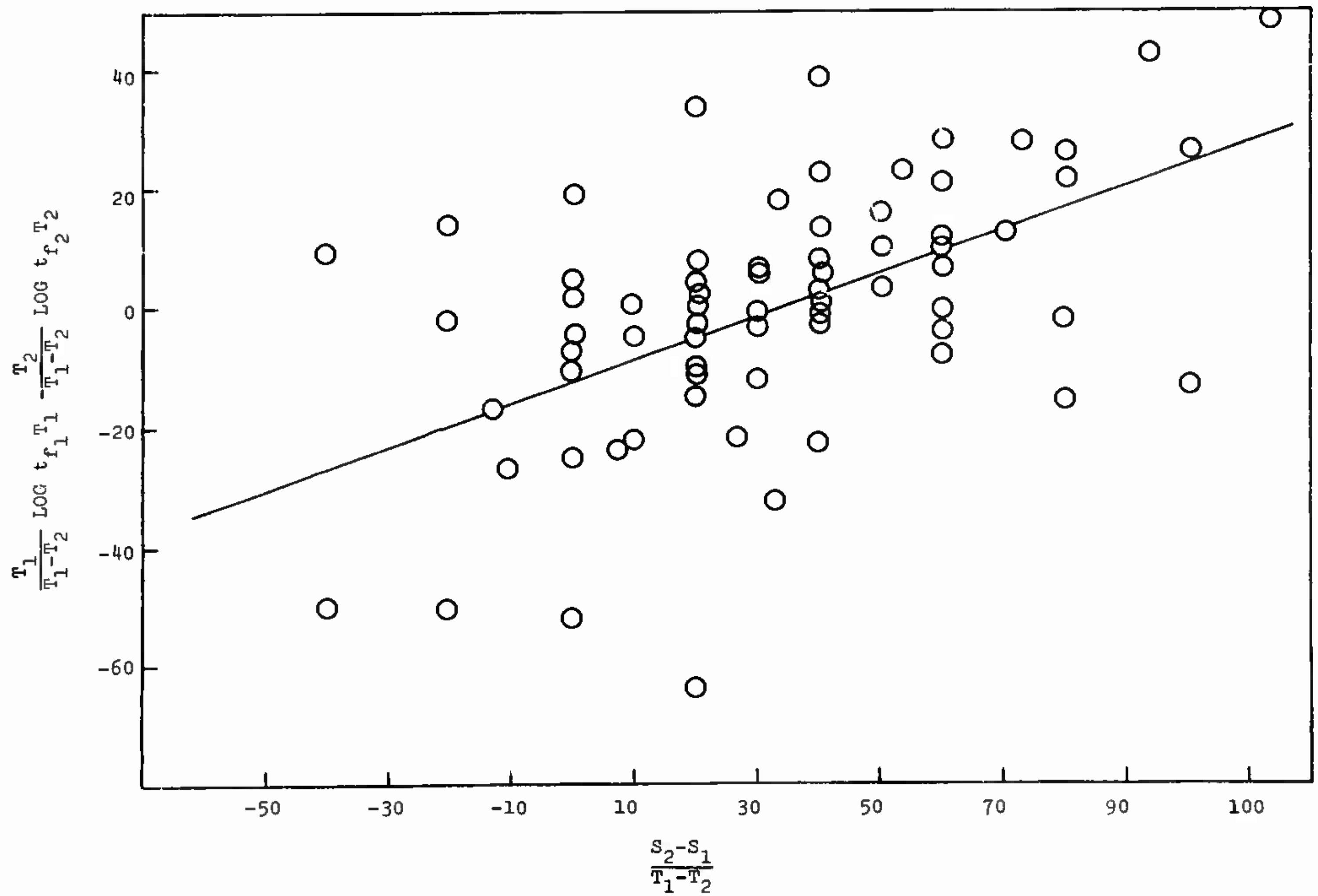

Fig 8 The data for AF126 adhesive at 20% relative humidity plotted according to Equation 8

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13. ABSTRACT

A reaction rate method was successfully used to predict failure times for adhesive bonds under constant stress at 90-95% and at 50% relative humidity. The method was found to be not very useful when the experiments were performed at 20% relative humidity. The results suggest that the method should be particularly useful under high humidity, bond degrading conditions such as exist in the tropics.

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